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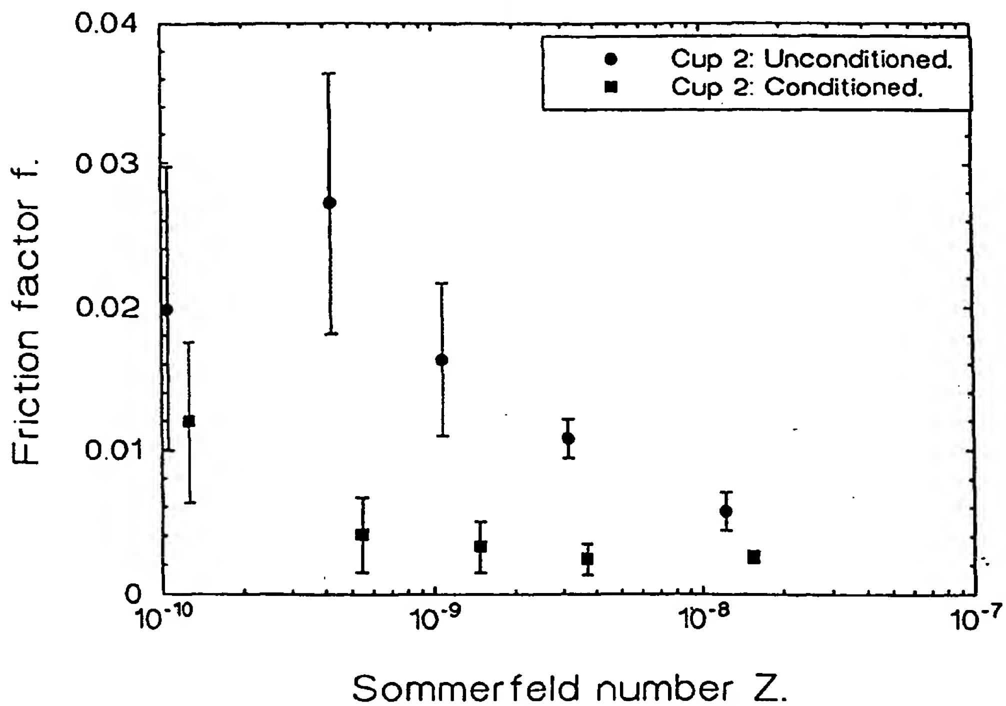
(54) **A process for improving start up and steady rate friction of soft/compliant polyurethanes**

(57) A process for improving start up and steady rate friction of soft/compliant polyurethanes in an aqueous lubricant which includes treating a polyurethane element in Ringers solution, an aqueous solution of phosphate buffered saline or de-ionized water.

Fig 2



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Description

This invention relates to a process for improving start up and steady rate friction of soft/compliant polyurethanes and to polyurethane elements which have been treated by the process. An important potential application for such treated material is in compliant layer bearings for example those used in artificial joint replacements, although it also has other applications.

Typically these artificial joint replacement bearings are relatively recent and rely on the use of soft/compliant polyurethanes (or other elastomeric materials) to improve the lubrication mechanism compared with conventional artificial joints. The concept of using a compliant polyurethane layer on the bearing surface of an artificial joint replacement is inspired by the natural synovial joint which has such a compliant layer, the articular cartilage. A combination of lubrication mechanisms have been proposed for synovial joints which result in fluid film lubrication, where the joint surfaces are completely separated by a thin film of lubricant. Currently most artificial joints are based upon metal on ultra high molecular weight polyethylene (UHMWPE), ceramic on UHMWPE or metal on metal material couples. These bearings are far less compliant than the natural joint and hence operate in a mixed lubrication regime, with partial contact of the two bearing surfaces. This leads to higher friction, and wear of the bearing surfaces of conventional joints. In contrast, compliant bearings operate with fluid film lubrication and extremely low friction, and hence potentially negligible wear and a long implant life.

The design parameters for the construction of compliant layer bearings are known. Polyurethane elastomers have been the materials of choice for these bearings. Under conditions of cyclic loading and motion typical of the major load bearing joints in the human body there is much experimental evidence that this type of bearing will operate with extremely low friction, typical of fluid film lubrication. In contrast, it has been reported by Caravia et al that the use of compliant polyurethane layers in this application can result in unacceptably high friction values under conditions which combine heavy loading and low sliding velocities, i.e. at the onset of motion (start up friction).

The purpose of this invention is to address the important area of improving start up friction whilst maintaining effective fluid film lubrication during normal cyclic loading and motion.

The following definitions are used herein

Ringers solution	This is a material which comprises a sterile solution of sodium chloride, potassium chloride and calcium chloride in water. It contains in each 100 ml. not less than 323.0 mg. and not more than 354.0 mg. of sodium, not less than 14.9 mg and not more than 16.5 mg. of potassium, not less than 8.20 mg and not more than 9.80 mg of calcium; and not less than 523.0 mg and not more than 580.0 mg of chloride.
coefficient of friction (μ):	the ratio of tangential frictional force to the normal load for a plane surface.
friction factor (**f**):	the ratio of the product of frictional torque (**T**) and cup radius to the normal load for the cupped geometry considered in this study, during steady state motion.
frictional torque (**T**):	the torque required to resist rotation of the compliant layered cup about an axis perpendicular to the axis of loading, under the normal load and motion conditions.
start up friction factor ($\mathbf{f_s}$):	friction factor (**f**) at the onset of motion.

According to the present invention a process for improving start up and steady rate friction in an aqueous lubricant of soft/compliant polyurethanes includes treating a polyurethane element in Ringers solution, an aqueous solution of phosphate buffered saline or de-ionized water.

Preferably the process includes treating the element in a heated bath containing the respective aqueous solution at a constant temperature between 30°C and 65°C, for example, good results have been obtained by treating the element at a temperature of 37°C for 96 hours.

The invention also includes a polyurethane element which has been treated by the process set forth.

The element can be or form part of a surgical or medical device which contacts body tissue and fluids, for example a prosthetic device, a stent, a catheter or an angio plastic balloon.

The devices referred to above all operate with an aqueous lubricant provided by the sinovial fluid in the human body.

As mentioned above material treated by the process can be used as a bearing surface and thus a prosthetic device according to the invention can have a bearing surface at least part of which is formed from a polyurethane element which has been treated by the method set forth above.

The prosthetic device can have a first bearing surface formed from the treated material and a second co-operating surface formed from, for example, metal or ceramic. The metal can be cobalt chrome steel, or similar metal or alloy used in implantable medical devices, and it can be provided with a diamond-like carbon (dlc) coating.

When applied to, for example, a hip joint the first treated surface can be provided on an acetabular cup and the second co-operating surface can be the co-operating ball head of the implant.

The invention can also be applied to, for example, tibial bearings suitable for total knee replacements.

The invention can be performed in many ways and some embodiments will now be described by way of example and with reference to the accompanying drawings in which :

Figures 1 and 2 are graphs showing friction factors for two acetabular cups before and after treatment;

Figure 3 is a diagram showing start up friction factor against preload time;

Figure 4 is a graph showing start up friction for an unconditioned cup with CoCr head combination;

Figure 5 is a graph showing start up friction for an unconditioned cup with a dlc head combination;

Figure 6 is a graph showing start up friction for a conditioned cup with CoCr head combination;

Figure 7 is a graph showing start up friction for a conditioned cup with dlc head combination;

The present invention addresses the issue of improving start up friction of compliant bearings designed for orthopaedic applications and other uses whilst maintaining effective fluid film lubrication mechanism under normal cyclic loading and motion.

The evaluation of the frictional properties of compliant layers referred to herein describes the properties of both "dry" contacts, and those lubricated with a low viscosity lubricant, i.e. pathological pseudo synovial fluid. The friction properties of the bearings have been measured on a machine which simulates the loads and motions experienced at the hip joint both at the start and during steady state motion.

In order to evaluate the invention the process was applied to polyurethane acetabular cups and these were preconditioned under a variety of different aqueous buffer systems or de-ionized water. The acetabular cups were typically treated in a heated bath which contains a respective aqueous solution at a constant 37°C for 96 hours. Further improvements can be realised by a shorter period at higher temperatures up to a maximum of 65°C. After this period the cups were removed, rinsed in de-ionized water, then cleaned by ultrasonication for 15 minutes. The cups were then tested directly or sterilized by gamma irradiation. Post-treatment of the cups can be normally packaged and irradiated or a combination of these processes.

In order to provide a diamond-like carbon (dlc) coating on a femoral head element a conventional 32 mm CoCr femoral head (manufactured by Howmedica) was treated using a commercial diamond like carbon process i.e. plasma assisted chemical vapour deposition (PA-CVD) to yield a coherent dlc coating over the articulating surface of the femoral head. The femoral head was used in the start up friction experiments described below, and as before provided an improvement in the start up friction in all cases;

(a) with the unconditioned compliant layer acetabular cup;

(b) after conditioning of compliant layer acetabular cup.

Frictional measurements (dry) were made with a simulator to measure the frictional torque developed in a hip joint under cyclic loads and motions typical of physiological conditions. The machine used is similar to that described by Unsworth, A. Dowson, D. Wright, V. (1974a) (The frictional behaviour of human synovial joints - Part 1: Natural joints. Trans. ASME: J. Lub. Tech., **74-Lub-38**). This apparatus is housed at Durham University, England. The apparatus consists of three main systems; which applied the joint load, drove the motion and measured the resulting frictional torque. The test hip joint was mounted with its centre of rotation incident with the centre of rotation of the simulator. The components were anatomically inverted, that is with the femoral head above the acetabular cup. A load of 1,000 N was used to protect the piezo electric transducer used in the simulator. Untreated (unmodified as manufactured) acetabular cups were used and the result is shown in Table I below.

Table 1 .

Dry friction factors of common counterfaces with candidate polyurethanes compliant layers.				
Polyurethane layer	CoCr Head		Ceramic Head	
	mean	s.d.	mean	s.d.
CSIRO	1.07	0.12	0.83	0.17
Corethane	1.01	0.18	1.02	0.13
Chronoflex	0.98	0.08	0.95	0.12
Tecoflex	0.88	0.13	0.94	0.14
Tecothane	0.77	0.30	0.93	0.17

The results showed that with typical polyurethane layers the dry friction factor values were typically 0.8 to 1.1. A friction factor of 1.0 would result in a frictional torque of approximately 30 Nm for an applied load of 2 kN acting to rotate a 32 mm diameter acetabular cup. This approaches the value of 100 Nm, reported by Anderson et al. as the static torque required to dislodge a well fixed cemented prosthesis.

Consequently, should the bearings run dry or intimate contact between the bearing surfaces occur, the level of friction generated under these conditions with untreated compliant layer bearings would be sufficiently high to risk accelerated loosening and could result in early failure.

Frictional measurements with steady state lubrication using two different acetabular cups, cup 1 and cup 2, was then carried out.

Steady state lubrication was assessed using two different acetabular cups, cup 1 and cup 2. Initially the cups were tested, after which the cups were conditioned in Ringers solution for 96 hours. Water based carboxyl methyl cellulose lubricants were used, with viscosity's ranging from 0.001 Pas (distilled water) to 0.1 Pas. These fluids were chosen as they have similar rheological properties to synovial fluid. The steady state lubrication regime was assessed by conducting Stribeck analyses for each case; the results are given in Figures 1 and 2.

Conventional joints have friction factors which typically range from 0.05 with lubricant viscosity's of 0.001 Pas, to 0.01 with lubricant viscosity's of 0.1 Pas. Clearly both joints in the unconditioned state provide better lubrication with lower friction factors than conventional joints. Cup 1 exhibited extremely low friction factors throughout the range of lubrications used. These low friction factor values were at the lower limit of detection of the Durham hip function simulator. Conditioning cup 1 did not change its tribological performance; low friction factors were maintained. Cup 2 was manufactured to be tribologically inferior to cup 1, and so in the unconditioned state exhibits higher friction factors. However, the tribological performance of cup 2 was shown to improve considerably after conditioning, demonstrating clear advantages of the conditioning process for somewhat less than optimum bearings.

Frictional measurements for lubricated start-up friction were now carried out. During operation of the Durham hip function simulator, a preload of 2 kN was applied to mimic the effect of standing and loading an acetabular bearing without any flexion-extension motion. This was achieved by operating the simulator in the "reverse" loading mode. The "reverse" mode cycle started with a high load, and hence a delay in starting the motion enabled the test cups to experience a fixed preload of 2 kN for 1, 2, 5, 10 and 20 mins. The frictional torque during the first two cycles was measured, using water as the lubricant, for the head/cup combinations summarised in Table 2, and the results plotted against preload time in Figure 3.

Table 2 .

Start up friction factors.						
Cup	Head	Start-up factor at different duration's of 2 kN preload				
		1 min	2 min	5 min	10 min	20 min
Unconditioned cup	CoCr head	0.34	0.48	0.52	0.52	0.55
Unconditioned cup	dlc coated CoCr head	0.07	0.09	0.22	0.34	0.43
Conditioned cup	CoCr head	0.06	0.16	0.20	0.23	0.43
Conditioned cup	dlc coated CoCr head	0.08	0.17	0.20	0.30	0.29

Conditioning was conducted as described above.

In general the results show that as relative motion starts the frictional torque is high, but that this quickly reduces within one cycle, to the extremely low values expected from compliant layer bearings. There are two characteristics

which have been used to differentiate between the material couples, that is the initial friction factors given in Table 2 and Figure 3, and the rate at which the frictional torque decreases during the period of initial motion.

The unconditioned cup and cobalt chrome steel head develops very high frictional torque which remains high throughout the period of initial motion, Figure 4. If a dlc coated head is used with the same unconditioned cup then the initial frictional torque is lower (especially under shorter preload duration) Figure 5, and it reduces still further as fluid is entrained during the stance phase.

The conditioned cup, figures 6 and 7, develops initial frictional torque values to the unconditioned cup/dlc head combination. However the frictional torque quickly reduces to a lower near constant value for the remainder of the cycle.

Caravia et al. assessed start-up friction developed between a thin polyurethane layer and several types of indenter using a pin on plate friction rig. A constant contact stress of 2 MPa and a sliding velocity of 8 mms-1 was used. The indenter was loaded for between 5 s and 400 s and the peak friction measured using water as a lubricant. In contrast, this simulator experiment used a dynamically applied load with a maximum contact stress of 7.3 MPa, a sinusoidal sliding velocity of maximum 34 mms^{-1}, and a preload of 2 kN applied for between 60 s and 1200 s.

Caravia et al. showed that the start-up friction increased with increasing preload time up to 80 s, after which they suggested the squeeze film action reached equilibrium and the friction increased no further. They reported higher values of start-up friction than this study, i.e. coefficients of friction between 0.6 and 1.1 for similar modulus material at 160 s preload. They also suggested that the surface energy of the bearing counter face could also be an important factor.

The experimental results of conditioned elements according to the present invention can be summarised:

1. Conditioning of the compliant layer cups provides for enhanced (or reduced) start up frictional performances and reduces the steady state friction.

2. Dlc coated head gives a slightly better performance than the uncoated head.

This work suggests that through the application of these inventions, either alone or in combination, lead directly to:

1) A significant reduction in start up friction.
2) A reduction in the effect of static preload on the frictional torque in the initial phase of motion.

These important results are critical to the long term performance of these bearings, since in contrast to the results presented by Caravia et al. which suggests start up friction may limit the lift of such devices, these inventions significantly reduce this potential problem.

It was observed during the experiments described above that the affects of conditioning the compliant bearing acetabular cups in Ringers solution or phosphate buffered saline (PBS) or de-ionised water improved both the start up friction and the steady rate friction characteristics. The frictional changes were related to an affect of surface re-organisation that occurs both within the bulk and at the surface of these polyurethane materials. These changes have been examined by the techniques of surface analysis such as ATR-fourier transform infra-red spectroscopy (ATR-FTIR), dynamic contact angle (DCA) and water uptake studies. Thus the process to promote these beneficial changes was optimised.

These significant improvements in the start up and steady state friction have been achieved using the processes of the invention, either alone or in combination. The application of these developments is primarily targeted at bearing systems for joint or surface replacement involving, but not limited to the hip, knee, elbow, shoulder and ankle. The major purpose is to apply for example, conditioning to modify the surface chemistry of linear polyurethanes to attain a hydrophilic surface that has low contact angle and hence wets with aqueous lubricants. This method of surface modification can not only be applied to compliant layer joints but also other medical devices that contact body tissues and fluids i.e. stents, catheters, angioplasty balloons etc.

A further application is associated with reducing friction in mechanical systems where sliding contacts are involved i.e. bushes (cylindrical or flat) that operate using predominantly aqueous lubricants, for example in tibial bearings suitable for total knee replacements.

Claims

1. A process for improving start up and steady rate friction of soft/compliant polyurethanes in an aqueous lubricant which includes treating a polyurethane element in Ringers solution, an aqueous solution of phosphate buffered saline or de-ionized water.

2. A process as claimed in claim 1 which includes treating the soft/compliant polyurethane element in a heated bath containing the respective aqueous solution at a constant temperature between 30°C and 65°C.

3. A process as claimed in claim 1 or claim 2 in which the temperature is 37°C for 96 hours.

4. A polyurethane element which has been treated by the process set forth in any one of the preceding claims.

5. A polyurethane element as claimed in claim 4 which is or forms part of a surgical or medical device which contacts body tissues and fluids when in use.

6. A polyurethane element as claimed in claim 5 in which the surgical or medical device is a prosthetic device, a stent, a catheter or an angio-plastic balloon.

7. A prosthetic device having a bearing surface at least part of which is formed from a polyurethane element which has been treated by the method set forth in any one of preceding claims 1 to 3.

8. A prosthetic device as claimed in claim 7 in which a first bearing surface is formed from said treated material and a second co-operating surface is formed from metal or ceramic material.

9. A prosthetic device as claimed in claim 8 in which the metal is cobalt chrome steel.

10. A prosthetic device as claimed in claim 8 or claim 9 in which the second co-operating surface is provided with a diamond-like (dlc) coating.

11. A prosthetic device as claimed in any one of preceding claims 7 to 10 in which said first treated surface is provided on an acetabular cup and the second co-operating surface is the co-operating ball head of an implant.

Fig. 1

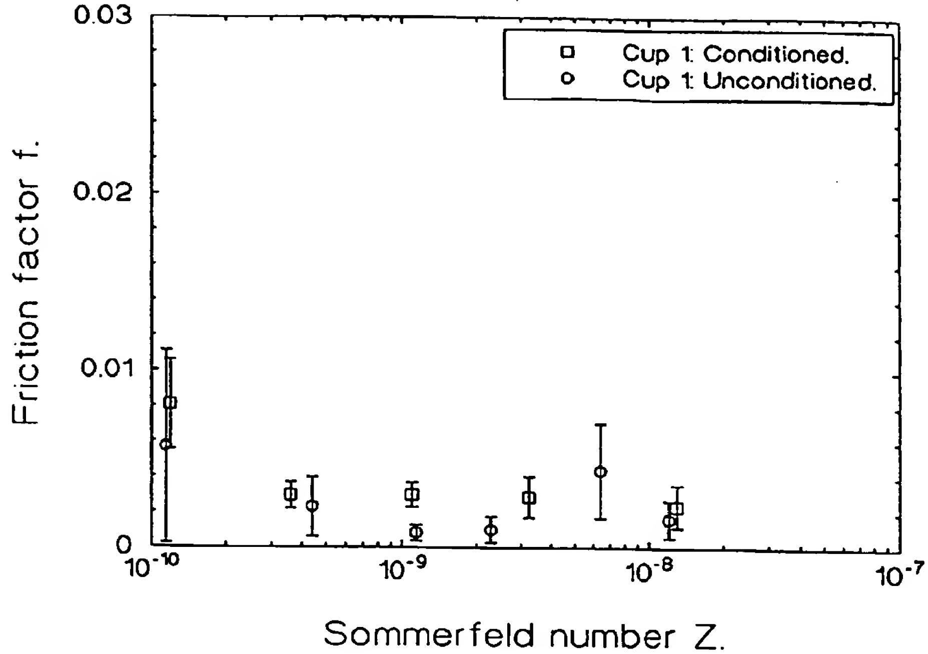
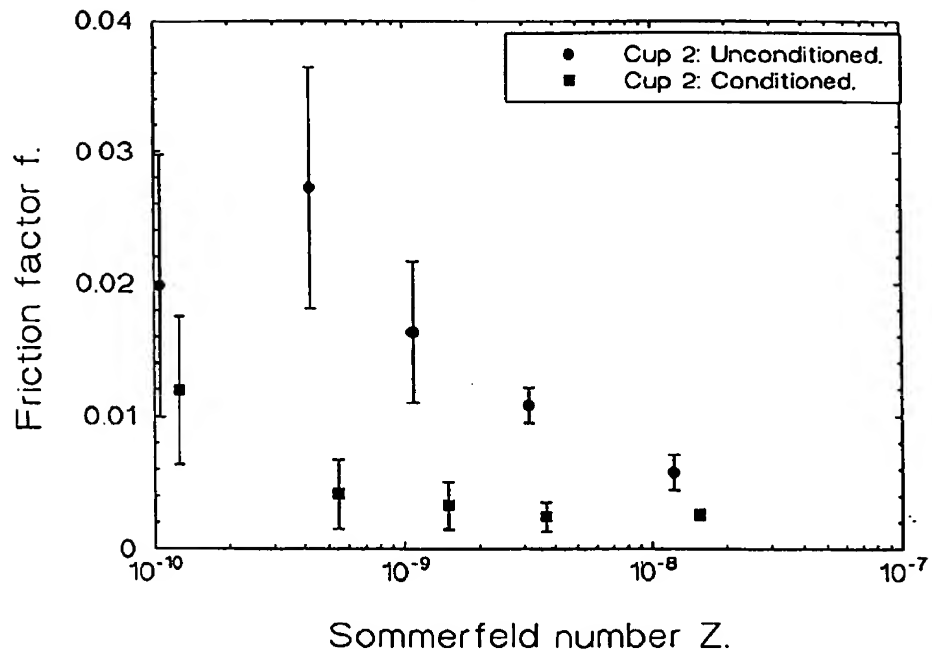

Cup 1: Conditioned.
Cup 1: Unconditioned.
Friction factor f.
0.03
0.02
0.01
0
10^{-10}
10^{-9}
10^{-8}
10^{-7}
Sommerfeld number Z.

Fig 2


Cup 2: Unconditioned.
Cup 2: Conditioned.
Friction factor f.
0.04
0.03
0.02
0.01
0
10^{-10}
10^{-9}
10^{-8}
10^{-7}
Sommerfeld number Z.

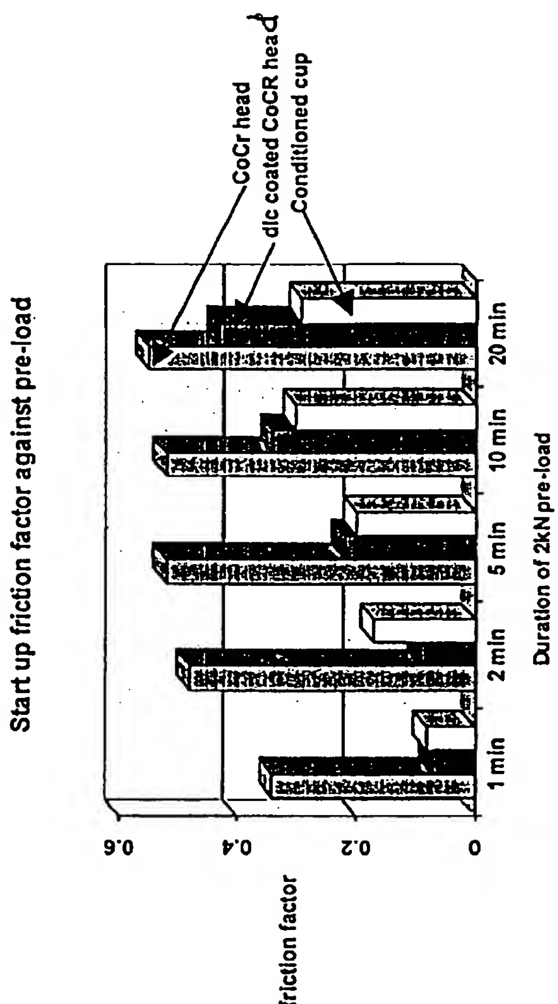

Start up friction factor against pre-load
friction factor
0.6
0.4
0.2
0
1 min
2 min
5 min
10 min
20 min
Duration of 2kN pre-load
CoCr head
dlc coated CoCR head
Conditioned cup

Fig 3

Fig 4

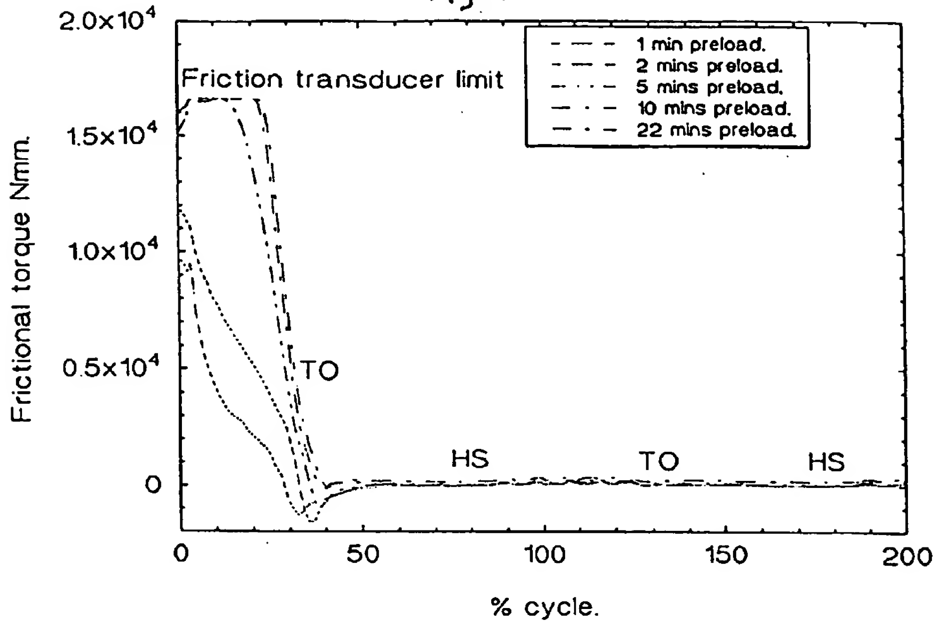

2.0x10^4
1.5x10^4
1.0x10^4
0.5x10^4
0
Frictional torque Nmm.
Friction transducer limit
1 min preload.
2 mins preload.
5 mins preload.
10 mins preload.
22 mins preload.
TO
HS
TO
HS
0
50
100
150
200
% cycle.

Fig 5

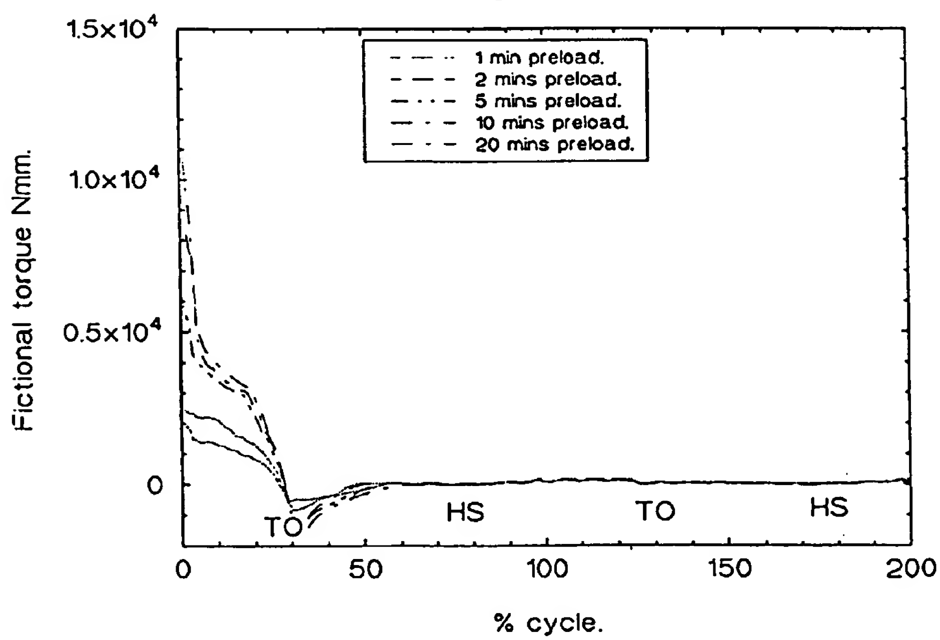

1.5x10^4
1.0x10^4
0.5x10^4
0
Fictional torque Nmm.
1 min preload.
2 mins preload.
5 mins preload.
10 mins preload.
20 mins preload.
TO
HS
TO
HS
0
50
100
150
200
% cycle.

Fig 6

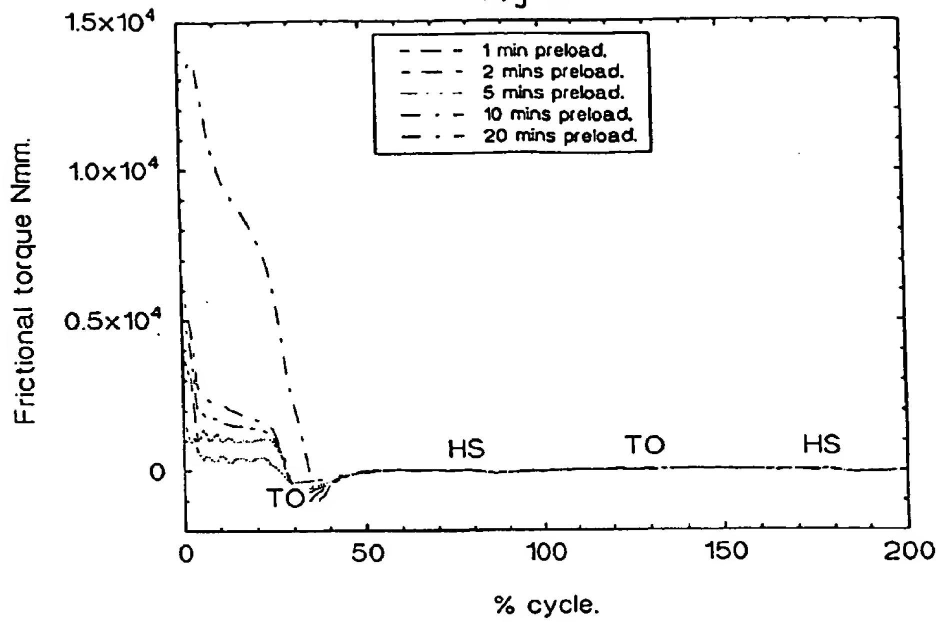
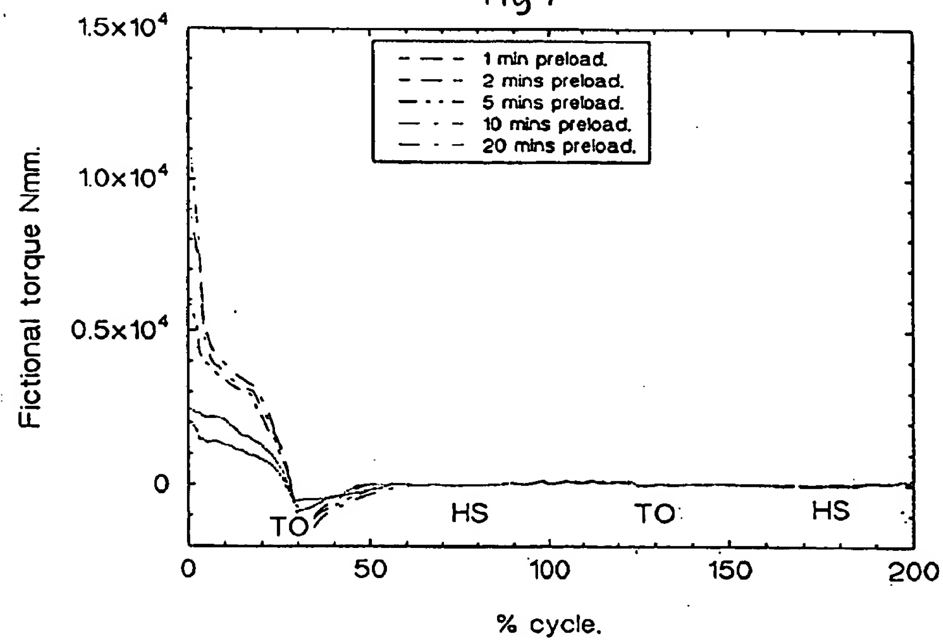

1.5x10⁴
1.0x10⁴
0.5x10⁴
0
Frictional torque Nmm.
1 min preload.
2 mins preload.
5 mins preload.
10 mins preload.
20 mins preload.
TO
HS
TO
HS
0
50
100
150
200
% cycle.

Fig 7


1.5x10⁴
1.0x10⁴
0.5x10⁴
0
Fictional torque Nmm.
1 min preload.
2 mins preload.
5 mins preload.
10 mins preload.
20 mins preload.
TO
HS
TO
HS
0
50
100
150
200
% cycle.